# NMR evidence for inhomogeneous density oscillations in the CuO chains of Ortho-II YBCO6.5

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## Abstract

Nuclear magnetic resonance (NMR) measurements of CuO chains of detwinned Ortho-II $YBa_2Cu_3O_{6.5}$ (YBCO6.5) single crystals reveal unusual and remarkable properties. The chain Cu resonance broadens significantly, but gradually, on cooling from room temperature. The lineshape and its temperature dependence are substantially different from that of a conventional spin/charge density wave (S/CDW) phase transition. Instead, the line broadening is attributed to small amplitude static spin and charge density oscillations with spatially varying amplitudes connected with the ends of the finite length chains. The influence of this CuO chain phenomenon is also clearly manifested in the plane Cu NMR.

Common to all cuprate superconductors, the $CuO_2$ planes have been the focus of much scrutiny for their essential role in the phenomenon of high temperature superconductivity (HTSC), including in the $YBa_2Cu_3O_{6+x}$ (YBCO6+x) family, whose layered structure also contains layers of quasi-one-dimensional (quasi-1D) CuO chains. In addition to acting as a charge reservoir for the planes in YBCO6+x, the chains have their own interesting properties due to their low dimensionality. In fact after almost two decades, there is still no consensus on either the ground state or the low energy excitation spectrum of the chains in YBCO6+x[1]. The behavior of quasi-1D correlated electrons has been the subject of intense study over the past couple of decades from both theoretical and experimental points of view, owing to the diversity of their electronic/magnetic properties as well as their amenability to exact calculation[2]. For example, insulating S=$\frac{1}{2}$ Heisenberg antiferromagnetic (AF) copper-based systems (with chain, ladder and plane topology) have been investigated recently in relation to the HTSC cuprates[3]. Due to the difficulty in doping these compounds, the main results have been to establish the detailed magnetic phase diagram, e.g. in $Sr_2CuO_3$[4]. Doped AF quasi-1D CuO chains in YBCO6+x are an interesting alternative to these commonly studied insulating chains. In HTSC cuprates, the static AF insulating ground state of two dimensional $CuO_2$ planes is destroyed easily by doping mobile carriers into these planes[5]. It is also important to investigate whether the magnetic properties of CuO chains play an equally crucial role in determining the properties of adjacent doped planes in YBCO6+x cuprate.

There are several oxygen ordered phases of YBCO6+x at certain fractional stoichiometries x. One such structure is the Ortho-II phase of YBCO6.5 which has full CuO chains alternating with empty chains. To the extent that the CuO chains are weakly coupled to the $CuO_2$ planes, the quasi-1D nature of the chains makes them susceptible to the formation of S/CDW's. The effective dimensionality of the CuO chains in YBCO6+x is determined by a hopping matrix element for mobile charges between the chains and planes (a process similar to the interlayer coupling which has also been the focus of much recent debate in relation to HTSC[6]). In low dimensional metallic systems, the formation of a S/CDW state is due to the topological enhancement of Fermi surface nesting, which becomes perfect in the limit of 1D. Although the relevance of a Fermi liquid picture is not at all clear in the cuprates, charge oscillations have indeed been observed in the CuO chains by nuclear quadrupole resonance (NQR)[7] in YBCO7 and STM[8] in YBCO6+x. In YBCO7, the Ortho-I phase of YBCO6+x,

the chains and planes are apparently coupled strongly enough that the charge oscillations in the chains induce charge oscillations in the planes of similar magnitude[7]. Thus the present work on highly ordered stoichiometry Ortho-II YBCO6.5 provides an important opportunity to examine not only a more isolated CuO chain than YBCO7, but also the chain-plane coupling effects in the underdoped pseudogap regime, where the $CuO_2$ planes' response to perturbations is substantially different[9].

NMR spectroscopy is a unique probe in studying the microscopic properties of the $CuO_2$ planes and CuO chain layers both separately as well as with interactions, due to the "site sensitivity" of NMR, i.e. each crystallographically inequivalent Cu site in the unit cell produces a separate resonance, whose lineshape and spin relaxation properties reflect the local electromagnetic environment of that site. In this letter, we present a detailed NMR study of the static properties of the full chain Cu sites in Ortho-II YBCO6.5. The results demonstrate that the ground state of the chains is inhomogeneous in both electronic spin and charge density but *cannot* be described by a conventional S/CDW ordered state. Additionally, we find that the spin (charge) modulations in the chains induce small but measurable inhomogeneity in the planes.

High quality Ortho-II YBCO6.5 single crystals, $T_c$=62 K and $\Delta T_c$=0.6 K, were grown by a flux method in $BaZrO_3$ crucibles[10]. The crystals, in the form of (*ab*-plane) platelets several millimeters on a side and a fraction of a millimeter thick (*c*-direction), were mechanically detwinned. X-ray diffraction measurements indicate typical uninterrupted chain lengths of about 120 **b**[10]. Conventional spin-echo measurements were made using a homebuilt NMR spectrometer with the field, $\mathbf{H}_0$, oriented along each of the crystallographic axes for various temperatures and field strengths[11]. Because of the small size of the samples, considerable averaging was essential to obtain reasonable signal-to-noise. The NMR spectrum observed for each Cu isotope consists of four lines, corresponding to the four inequivalent Cu sites in the unit cell: full chain, empty chain, planar Cu adjacent to either the full chain or empty chain, hereon denoted by Cu(1F), Cu(1E), Cu(2F) and Cu(2E), respectively (see Fig. 1 in[11] for the crystal structure). Line assignments are based on a comparison of the Knight shift and quadrupolar parameters obtained for these four sites to the known values in YBCO6 and YBCO7[11]. To our knowledge, these are the narrowest and best-resolved resonances observed for any oxygen depleted YBCO6+x material, an indication of the high quality of the samples. At low temperatures, the central transition linewidths for the planar sites

Cu(2) is of order 0.1 MHz and that of the empty chain site Cu(1E) is somewhat less. In contrast, the Cu(1F) sites have a full width of order of 1 MHz at low temperatures. The much broader resonance observed for Cu(1F) implies a remarkable inhomogeneity in its local environment compared to the other sites. It is this inhomogeneity that is the main subject of this study.

The $^{63}$Cu(1F) lineshape for the applied field perpendicular to the chains ($\mathbf{H}_0||\mathbf{a}$) is shown as a function of temperature in Fig. 1(a). At low temperatures the line is broad. With increasing temperature the broad line *gradually* narrows while simultaneously a narrow line appears and increases in relative intensity at the expense of the broad line. A similar temperature dependence has also been observed for the applied field along the $\mathbf{b}$ and $\mathbf{c}$ axes. At the highest temperature for which data has been collected (250 K) most of the intensity is in the narrow line, but there is still a remnant of the broad line.

As CuO chains in Ortho-II YBCO6.5 are low dimensional, one might suggest the observed broadening at low temperatures is due to a transition to a S/CDW state. For a simple homogeneous 1D incommensurate S/CDW state, the NMR lineshape consists of two singularities separated by a frequency difference associated with the peaks and troughs of the density waves[12]. The singularities appear at the onset of S/CDW state and their separation (a measure of the order parameter) increases on cooling until the ordered phase is fully developed. Our data (see Fig. 1 as an example), however, indicates that two singularities expected from a simple homogeneous 1D incommensurate S/CDW state are absent in the Cu(1F) lineshape. In addition, the smooth evolution of the lineshape with temperature (30 to 250 K) is inconsistent with a homogeneous density wave phase transition characterized by a well-defined critical temperature $T_{DW}$[12]. In principle, one might expect that $T_{DW}$ could depend on chain length for any particular CuO segment; however, the average segment length is so large, that most of them would already be in the homogeneous limit. Hence, based on both the Cu(1F) lineshape and the temperature dependence of the measured spectra, we rule out such a transition taking place in CuO chains in Ortho-II YBCO6.5.

We find, on the other hand, that the Cu(1F) lineshape *is* consistent with presence of an spatially varying amplitude oscillation induced by the chain ends depicted in the inset of Fig. 1. We attribute the observed broad component of the Cu(1F) line to regions of the chains with large amplitude static oscillations, while the narrow component at high temperatures is identified with regions where this amplitude is small or zero, probably due
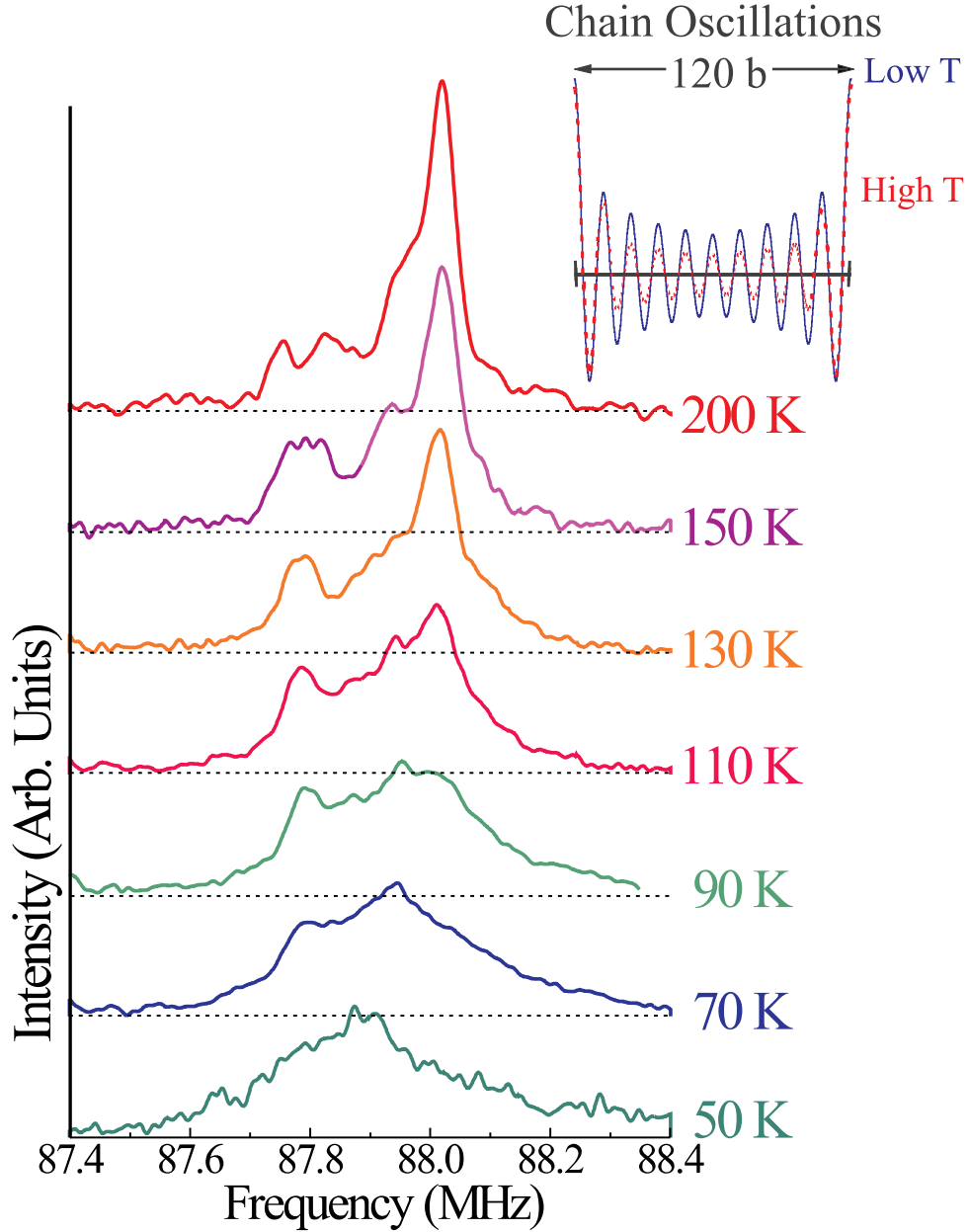
FIG. 1: Temperature dependence of $^{63}Cu(1F)$ lineshape measured at 7.7 T with $\mathbf{H}_0||\mathbf{a}$. Inhomogeneous density oscillations are depicted for low (solid line) and high temperatures (dash line) in the inset.

to dynamic averaging. The absence of the narrow line at low temperatures indicates that the oscillations have spread over the entire chain. The three-fold coordinated Cu site at the chain end must have a different local charge than other chain Cu sites as it only has one neighbouring oxygen in the chain instead of the usual two. Chain ends are thus effectively

impurities in the chains. In a conventional metal, due to the sharp cut-off in occupied conduction electron states at the Fermi surface, a charged impurity leads to a spatially oscillating static screening cloud of conduction electrons, the so-called Friedel oscillations[13]. Similarly, a magnetic defect in a metal gives rise to an oscillating spin polarization of the screening conduction electrons, i.e. RKKY oscillations. There are analogous effects in low dimensional *insulating* magnetic systems. Theoretical[14] and experimental[4] studies of insulating S=$\frac{1}{2}$ 1D Heisenberg AF chains reveal oscillations in the susceptibility near the chain ends. Thus one may also expect the doped S=$\frac{1}{2}$ chains in YBCO6.5 to have similar spin oscillations induced by the chain ends. Recently, Morr and Balatsky[15] have studied the electronic structure near impurities in chains of YBCO6+x coupled to the planes and have indeed found spatially varying amplitude spin/charge oscillations in the electronic density of states. Our experimental result confirms the presence of such oscillations in the CuO chains of Ortho-II YBCO6+x.

In general, the broadening of the Cu(1F) line can be due to inhomogeneity in *both* the local magnetic field (through the local magnetic susceptibility, to the local magnetic shift) and the electric field gradient (through the quadrupolar effects on the resonance). While the Knight shift distribution is the same first order for both transitions, the quadrupolar broadening of the central transition is second order in nuclear quadrupole frequency, $\nu_Q$, whereas it is first order for the satellite transitions[11]. Hence by comparing the lineshapes of the central and satellite transitions, one can establish limits on the extent of the distribution of the various quadrupolar and Knight shift parameters. Fig. 2 shows typical Cu(1F) spectra observed at low and high temperatures for both central and satellite transitions. It is clear that the central and satellite transitions exhibit approximately the same the linewidths. Our numerical simulations[16] further show that even large distributions in the quadrupolar parameters *cannot* simultaneously reproduce the linewidths of both the central and satellite transitions (see Fig. 2 (c) and (d)). Thus the majority of the broadening of the Cu(1F) resonance comes from a magnetic (Knight) shift distribution, with a much smaller contribution from quadrupolar broadening due to a distribution in the charge density. The simulations indicate that a distribution of 0.1-0.25 MHz in $\nu_Q$ can explain the observed linewidths of satellite and central transitions for all field orientations. Therefore, we do have evidence of *charge* oscillations, but our results show that they are very small in amplitude. This is *not* because $\nu_Q$ is insensitive to the local charge, in fact systematic studies of the role of the

Cu ion's valence on $\nu_Q$ have found that $\nu_Q$ is extremely sensitive, varying by about 20 MHz per hole[17]. Using this scaling, the distribution of $\nu_Q$ here corresponds to a static charge oscillation amplitude of about 0.5-1.25% of an electron per site.

We now consider the distribution in the Knight shift. There are two contributions to the Knight shift $K=K_s+K_{orb}$ where $K_s$ is the Knight shift due to the local spin susceptibility and $K_{orb}$ is the orbital shift (temperature independent shift due to a local electron screening of the magnetic field). It is known from previous measurements[18] of Cu(1F) in YBCO7 powder samples that $K_{orb}^{\mathbf{a}}\simeq1.2\%$, $K_{orb}^{\mathbf{b}}\simeq0.4\%$ and $K_s\lesssim0.2\%$ at 70 K. In contrast, the maximum extent of the broadening of our central line is $\simeq0.8\%$ along $\mathbf{a}$ and $\simeq1.3\%$ along $\mathbf{b}$ at 70 K, 7.7 T. Thus, since the orbital shift has the wrong symmetry, it is doubtful that a distribution of $K_{orb}$ is the predominant source of broadening. $K_s$ is too small by an order of magnitude[11] to account for these linewidths. The hyperfine coupling constants, on the other hand, do have the correct symmetry for all directions. Using estimates for the on-site and transferred hyperfine coupling constants from Mila and Rice[19], $(A+2B)_{\mathrm{a}}=80$ KOe/$\mu_B$ and $(A+2B)_{\mathrm{b}}=120$ KOe/$\mu_B$, we find that a 1.5% maximum polarization of the local moments can account for our spectra, assuming the chain local moments have the same magnitude as those in the planes, i.e. 0.6 $\mu_B$[20].

Finally, we discuss the effects of chain oscillations on plane Cu sites. The broadening of the plane Cu resonances follows that of Cu(1F), but is smaller in magnitude for Cu(2F) and smaller yet for Cu(2E). The similarity of the temperature dependence of the plane Cu broadening to Cu(1F) broadening is evident in plots of the plane Cu widths vs. the Cu(1F) rms moment[21], $\mathrm{M}_{rms}$, with temperature as an implicit parameter (see Fig. 3 for $\mathbf{H}_0||\mathbf{b}$ for an example). Linear behavior found for all field orientations, shows clearly that they all originate from the same phenomenon, namely the inhomogeneity of the full CuO chains. Additionally the decreasing magnitude of this effect for sites progressively further away from the CuO chains is strong evidence that the origin of the line broadening lies in the CuO chains. Other independent sources of broadening are reflected in the small nonzero intercepts. This is in contrast to YBCO7 where the $\nu_Q$ linewidth of both chains and plane sites suddenly increases below the superconducting transition *with the same magnitude*[7]. This qualitatively different behavior is likely a consequence of a stronger chain-plane coupling in YBCO7, which is also reflected in its less anisotropic electrical conductivity. In addition, unlike YBCO7, where the linewidths of both the chain and plane sites are constant on cooling
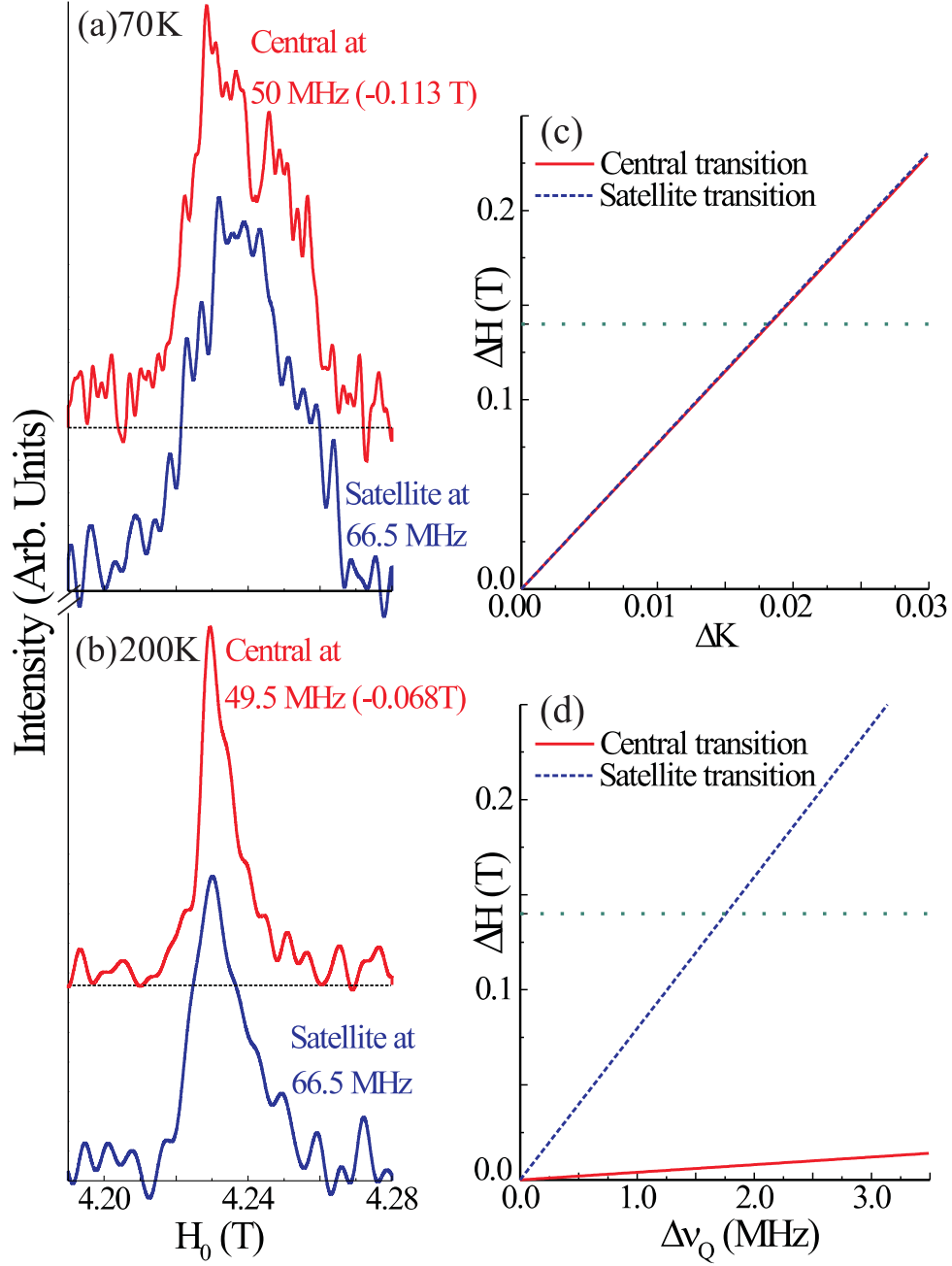
FIG. 2: Central and satellite $^{63}$Cu(1F) spectra taken at 4.2 T at 70 K (a) and 200 K (b) with $\mathbf{H}_0||\mathbf{b}$. The central transition spectra are shifted (by the amount shown on the graphs) to roughly align their center of gravity. The numerical simulations of the Cu(1F) resonance widths as a function of Knight shift (c) and quadrupolar (d) distributions. The horizontal dashed-line in (c) and (d) shows the maximum extent of the line observed for $\mathbf{H}_0||\mathbf{c}$.

until below the superconducting $T_c$, for Ortho-II YBCO6.5 large but gradual increase in the linewdith is observed on cooling. It has been suggested that in YBCO7 the Coulomb interaction between charge carriers is responsible for suppressing the CDW order, until the $CuO_2$ planes become superconducting. If this is the case, then the gradual increase indicates that a similar suppression effect of the charge/spin oscillations is not evident in Ortho-II YBCO6.5.
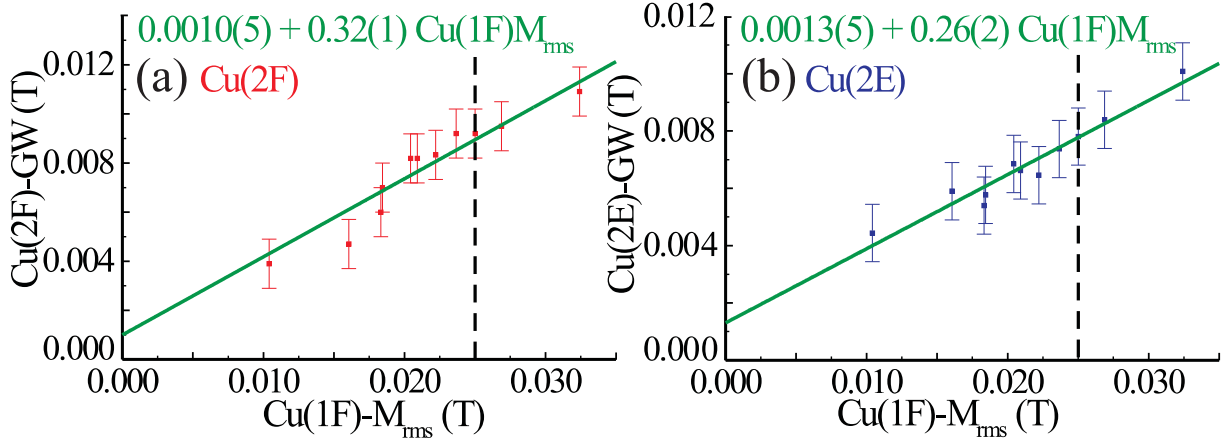


FIG. 3: A linear relation is found between the Gaussian widths of the planar Cu(2F) and Cu(2E) sites and Cu(1F) $M_{rms}$, (a) and (b) respectively, with $\mathbf{H}_0||\mathbf{b}$. The dash line is positioned at $T_c$. Similar linear behavior is also observed for the other field orientations.

We have investigated with NMR a system of weakly coupled chains and planes, namely Ortho-II YBCO6.5 and present strong evidence that standing waves of spin (and to a lesser extent charge) density oscillations with spatially varying amplitude form in the finite length chains at low temperatures. We find the oscillations are reduced gradually with increasing temperature. This inhomogeneous electronic state in the chains clearly influences the microscopic electronic structure in the planes. It is therefore important to understand this phenomenon in order to properly distinguish between behaviour arising in the 1D chains from the effects inherent to $CuO_2$ plane effects, such as the possible stripe phase.

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